Phase Studies of the Systems Synthetic Soap-Sodium Chloride-Water

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EXTENSIVE PHASE STUDIES have been made by McBain and collaborators in ternary systems of fatty acid soap, salt, and water. The purpose of the present paper is to report a similar investigation with synthetic soaps, mainly sodium secondary alkyl sulphates. The study was made in connection with problems concerning the preparation of solid synthetic soaps.

Experimental Procedure

Materials. The soaps investigated were sodium secondary C_8-C_{18}, C_{10}-C_{18}, C_{12}-C_{18}, and C_{14}-C_{18} alkyl sulphates[1] (molecular weights 300, 307, 313, and 333, respectively), all made by converting the corresponding olefins (cracked wax olefins mainly consisting of α-olefins) with sulphuric acid, and a number of pure synthetic alkyl sulphates, alkyl sulphonates, and alkylarene sulphonates.

The mixed alkyl sulphates were purified as follows: unsulphated organic material was removed by continuous extraction with a 5:1 mixture (by volume) of pentane and i-propyl alcohol. Sodium sulphate was precipitated by adding i-propyl alcohol until the mixture contained 92% volume of i-propyl alcohol. i-Propyl alcohol and water were removed from the filtrate by evaporation in vacuum at a temperature below 50°C.

Method. On adding sodium chloride to the soap solutions, separation into two or three layers occurs at temperatures of 40°C. or higher. In order to determine the concentrations of soap and sodium chloride at which phase changes occur at a certain temperature, three different methods used by McBain have been employed, the so-called synthetic, delimiting, and analytical methods (1). The first (which consists in observing the temperature at which phase changes occur in systems of known composition) could only be employed to find the boundary of the isotropic region because in other regions the temperatures necessary for obtaining a homogeneous solution were too high and decomposition occurred. Owing to decomposition, very long settling times, as are often used in the analytical method, were not permissible either. The procedure therefore used in most cases was the delimiting method, consisting in observing the phases present in mixtures containing a certain amount of soap and increasing quantities of salt. Decomposition could easily be detected by a lowering of pH.

Most of the experiments were done in calibrated 10-ml. glass tubes at temperatures above the "Kraft"

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[1] Mixtures of secondary alkyl sulphates with a number of carbon atoms ranging between C_8 and C_{18}, C_{10} and C_{18}, etc.

TABLE I

Results of Delimiting Experiments in the System Sodium C_8-C_{18} Alkyl Sulphate-NaCl-H_2O

Temperature: 50°C.

% soap	5.0	10.0	15.0	20.0	30.0	40.0	Phases present at equilibrium
% NaCl added	17.0 17.5	17.0	16.0	14.0 14.5	12.0	9.0	Homogeneous nigre
	↓	17.5	17.0	15.0	12.5 13.0	9.5 10.0	Nigre + neat soap
	18.0 19.0	↓		↓		↓	Nigre + lye
	20.0 21.0	18.0 19.0 20.5		16.0[a] 17.0[a] 18.0[a]		11.0[a] 12.0[a]	Nigre + neat soap + lye
	22.0	21.0 22.0		19.0		13.0 14.0[b]	Neat soap + lye
		23.0 24.0		20.0 21.0		15.0[b] 16.0	Kettle wax or curd soap + lye
		25.0		22.0		17.0	Kettle wax or curd soap + lye + solid NaCl
Temperature: 80°C.							
% NaCl added	17.0	17.0	16.0	16.0	12.0 12.5	9.0	Homogeneous nigre
	↓	↓	↓		13.0 14.0	10.0 11.0 12.0	Nigre + kettle wax or curd soap
	18.0	17.5 18.0 19.0	16.5		↓	↓	Nigre + lye
		20.0 21.0 22.0		16.5 17.5	15.0 16.0	13.0	Nigre + kettle wax or curd soap + lye
		23.0 24.0			17.0 18.0	14.0	Kettle wax or curd soap + lye
		25.0			19.0		Kettle wax or curd soap + lye + solid NaCl

[a] It was difficult to see whether lye was present or not.

[b] Gradual transition from the doubly refracting translucent neat soap to the granular opaque kettle wax (or curd soap). This is in agreement with phase theory which demands that a 3-phase region neat soap-kettle wax (or curd soap)-lye must be present.

point, the temperature at which a more or less abrupt increase in solubility occurs. With the C_8-C_{18} and other mixed alkyl sulphates a temperature of at least 45°C. was needed, with the pure synthetic sulphates of at least 65°C., and one of at least 70°C. with the sulphonates. As mixed alkyl sulphates are a mixture of compounds containing alkyl groups of different length, it is not entirely permissible to consider the substances as consisting of one component. Nevertheless the three-component phase diagrams (sodium alkyl sulphate-NaCl-water) of mixed alkyl sulphates (if treated as consisting of one component) and pure alkyl sulphates do not differ in their essential aspects. Earlier investigators found the same for mixed fatty acid (commercial) soaps.

Results and Discussion

a. *Phase Diagrams of Sodium Secondary C_8-C_{18} Alkyl Sulphate-NaCl-Water.* The data obtained for purified secondary C_8-C_{18} sodium alkyl sulphates are recorded in Tables I, II, and III, and in Figures 1 and 2 for 50°C. and 80°C. The figures show several two- and three-phase regions. At least three kinds of solid phases are present. The phase diagram and the phase properties are, qualitatively, very similar to those of fatty acid soaps. Also with sodium alkyl sulphates middle soap is a very clear birefringent, liquid-crystalline phase. This could easily be seen in the test tubes by using two crossed Polaroid glasses. The middle soap is a rubber-like mass that can be torn to threads and strings. It is hard to dissolve and, on cooling, does not pass into curd fibers, the stable phase at room temperature, or only does so very slowly. The neat soap, which contains a higher percentage of active matter (about 75%), is also a birefringent, liquid-crystalline phase; it is more or less fluid and translucent. Curd fibers are the common crystalline phase at room temperature. Sometimes they are granular in appearance; by microscopic observation at 50°C. it was found that this was always the case when curd phase was obtained by salting out. It is quite possible however that in these cases it was not curd phase but kettle wax that separated out (see later). Curd soap or kettle wax is difficult to separate as a single phase. After centrifuging it still contains water between the particles.

TABLE II

Results of Analysis of Separated Phases of Sodium C_8-C_{18} Alkyl Sulphate

	Composition of total system	% NaCl in lye	% soap in lye
Lye at 50°C.	10.0% soap, 22.5% NaCl (3 phases)	22.9	≦0.3
	10.0% soap, 21.0% NaCl (2 phases)	24.0	≦0.3
	20.0% soap, 18.0% NaCl (3 phases)	22.2	≦0.3
	20.0% soap, 19.0% NaCl (2 phases)	24.6	≦0.3
Lye at 80°C.	10.0% soap, 22.0% NaCl (3 phases)	23.9	≦0.3
	10.0% soap, 23.0% NaCl (2 phases)	24.6	≦0.3
		Composition of lye	Composition of nigre
Nigre-lye region at 50°C.	5.0% soap, 19.0% NaCl	20.9% NaCl, < 0.3% soap	18.1% NaCl, 8.0% soap
Nigre-lye region at 80°C.	10.0% soap, 19.0% NaCl	21.5% NaCl, < 0.3% soap	17.3% NaCl, 19.1% soap
Neat soap at 50°C.	Soap content of neat soap 69-79% NaCl content of neat soap 1½-4%	From a great number of experiments in which neat soap separated out.	
Kettle wax or curd-soap at 50° and 80°C.	Composition varying from 45-80%, dependent on the intensity of centrifuging and filtration.		
Middle soap at room temperature	Composition of total system: 47.2% soap, no NaCl. After 2 months' storage the separated phases (metastable) had the composition: 46.8 and 48.1% soap.		
3-phase region	See Table IV.		

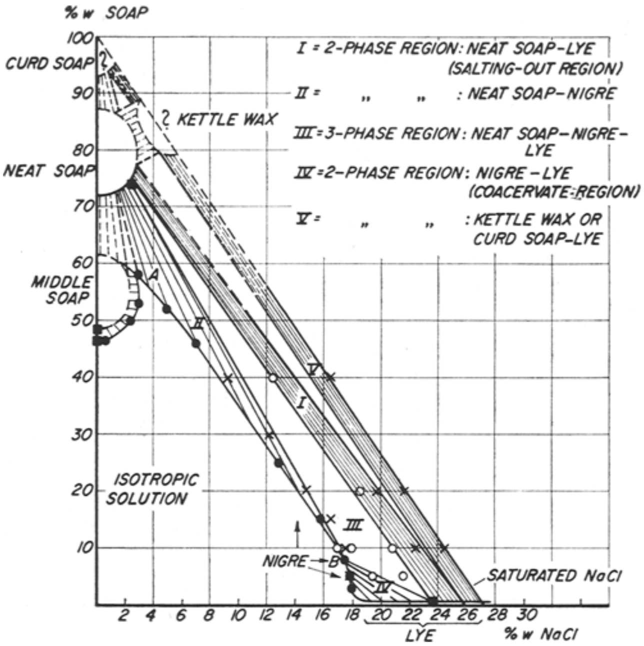

FIG. 1. Phase diagram of sodium C_8-C_{18} alkyl sulphate-NaCl-H_2O at 50°C.

- ● points on the boundary of the isotropic region, calculated by the synthetic method
- ○ points on the boundary of the 3-phase region III, calculated by the delimiting method
- × points on other boundaries, calculated by the delimiting method
- ■ points calculated from analysis.

Dashed lines: only based on analogy with fatty acid soaps.

The diagrams show that the addition of NaCl to a sodium C_8-C_{18} alkyl sulphate solution, with an active matter content less than that corresponding to point B, results in a separation, at about 17½% NaCl, of two liquid phases. This is the region which, according to the definition of Bungenberg de Jong (separation of two liquid phases in a colloidal solution), may be called the coacervate region (IV). The upper layer is called nigre and contains nearly all the soap; the lower layer is called lye. The lye contains somewhat more NaCl than the nigre, and its soap content is

TABLE III

Results of Synthetic Experiments with Sodium C_8-C_{18} Alkyl Sulphate at 50°C. and 80°C. T_i = Temperature in °C. at Which Isotropic Solution Separates a Second Phase

% soap	% NaCl	T_i	% soap	% NaCl	T_i
2.50	17.9	>95 and 45[a]	59.0	2.5	63
2.50	17.8	87 and 38[a]	61.0	2.1	69
5.0	17.7	>95 and 46[a]	61.6	2.0	>95
7.5	17.5	89 and 47[a]	61.6	1.8	>95
8.0	17.5	>95 and 49[a]	60.0	1.9	81
9.9	17.0	49	58.0	2.2	79
10.0	17.2	>95	58.0	2.1	82
15.0	15.8	49	57.0	2.9	56
25.0	12.8	52	55.0	3.0	61
37.5	9.4	58	54.1	2.3	85
44.0	8.3	79	53.0	3.1	58
46.0	7.0	53	50.0	2.0	75
50.0	6.2	85	49.8	2.5	46
52.0	4.8	41	49.2	2.0	69
52.0	5.3	69	49.0	1.0	82
54.0	4.7	73	46.3	0.5	50
58.0	2.9	51	48.0	0	>95
58.0	3.2	78	47.0	0	73
58.0	2.5	65	46.4	0	50

[a] Between the two temperatures the solution becomes clear again; this phenomenon must be due to the partial overlapping of the 2-phase regions at 50°C. and 80°C.

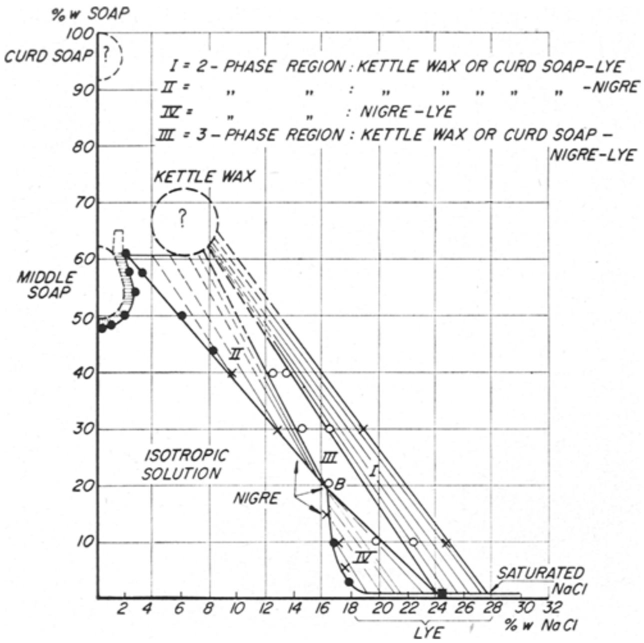

FIG. 2. Phase diagram of sodium C_8-C_{18} alkyl sulphate-NaCl-H_2O at 80°C.

- ● points on the boundary of the isotropic region, calculated by the synthetic method
- ○ points on the boundary of the 3-phase region III, calculated by the delimiting method
- × points on other boundaries, calculated by the delimiting method
- ■ points calculated from analysis.

Dashed lines: only based on analogy with fatty acid soaps.

very low. It is equal to the critical micelle concentration (not sharply defined in mixed alkyl sulphates), that is to say, the small amount of soap is only present in the non-micellar form. In the middle of the isotropic region the solution may become highly viscous or set to an isotropic jelly, but this is not a separate phase. If more NaCl is added first, the 3-phase region III (neat soap-nigre of composition B-lye) is reached and then the 2-phase region I (neat soap-lye). If the soap solution has an active matter content higher than that corresponding to point B, addition of NaCl causes separation into neat soap and nigre (region II). If more NaCl is added, the same sequence as with lower soap concentrations is found.

As to the determination of the boundaries of the different regions, the following may be stated. The boundary of the isotropic region was determined mainly by the synthetic method. Data obtained with the delimiting method are in good agreement with the former (see Figures 1 and 2). The other boundaries were determined by the delimiting method. Data obtained with the analytical method in the 3-phase region neat soap-nigre-lye, in comparison with those of other methods, showed 1 to 3% higher NaCl contents of the nigre and 2½ to ½% lower NaCl contents of the lye, dependent on the initial NaCl content of the mixture (see Table IV); therefore a 3-phase region is, according to the analytical method, much narrower than according to the other methods; moreover it is not invariant as it would be if only three components were present. This proves that it is not quite permissible to consider the mixed ester salt as consisting of one component only.

For pure synthetic alkyl sulphates all methods are in agreement; the 3-phase region is always very narrow. An experiment with a mixture of two of these synthetic alkyl sulphates with different alkyl chains showed that the 3-phase region is widened (Table V).

TABLE V

Influence of Mixing on the 3-Phase Region

	NaCl content of 10% ester salt solutions at which 3 phases are present
Sodium n-hexadecyl-2-sulphate	5½-6½% NaCl
Sodium n-dodecyl-2-sulphate	only 20½% NaCl
50:50 mixture of sodium hexadecyl-2 and dodecyl-2-sulphate	18-19½% NaCl

This is a second, although indirect, proof that the difference in results between the analytical and other methods in the case of the mixed alkyl sulphates is not due to insufficient phase separation or slow establishment of equilibrium, but mainly to the fact that the 3-phase region is not invariant.

According to the phase theory the above phenomena must be accompanied by a fractionation of mixed alkyl sulphates, that is to say, the neat soap must contain more of the less soluble alkyl sulphate than the nigre.

The temperature has a marked influence on the phase diagram of sodium C_8-C_{18} alkyl sulphates. At 50°C. the alkyl sulphate concentration of point B is about 8%, at 80°C. it is about 19% (see Figures 1 and 2). The 2-phase region IV is greater at 80°C. than at 50°C. The most striking difference is that at 80°C. the salted-out alkyl sulphate only seems to contain 40-50% of active matter. This phase does not have the appearance of neat soap (translucent and doubly refracting) but is a suspension of granular soap. Centrifuging or filtration causes the active mat-

TABLE IV

Comparison of Different Methods for Determining the Composition of the Two Liquid Phases for the 3-Phase Region Neat Soap-Nigre-Lye

Soap	Method	Initial composition of the mixture	% NaCl in		% soap in	
			Nigre	Lye	Nigre	Lye
Sodium C_8-C_{18} alkyl sulphate	Delimiting		17.5	23.5	....	....
	Synthetic		17.4	....	8.0	....
		10% soap + 18.5% NaCl	18.3	21.0	8.2	0.3
	Analytical	10% soap + 20.5% NaCl	20.6	22.9	8.2	0.3
Sodium C_{10}-C_{18} alkyl sulphate	Delimiting		13.0	20.0	....	....
	Synthetic		13.0	....	8.0	....
	Analytical	10% soap + 15.0% NaCl	14.8	17.1	9.0	0.1
Sodium C_{12}-C_{18} alkyl sulphate	Delimiting		11.0	17.0	....	....
	Synthetic		11.0	....	9.0	....
	Analytical	10% soap + 13.0% NaCl	12.9	14.9	10.1	0.1
Sodium C_{14}-C_{18} alkyl sulphate	Delimiting		7.0	14.5	....	....
	Synthetic		6.8	....	9.0	....
	Analytical	10% soap + 9.0% NaCl	8.4	10.3	10.3	0.1

TABLE VI

Results of Delimiting Experiments in Systems Sodium Alkyl Sulphates-NaCl-H₂O at 50°C.

	Sodium C_{10}-C_{18} alkyl sulphate					Phases present at equilibrium
% soap	5.0	10.0	20.0	30.0	40.0	
% NaCl added	13.0	12.0	10.0			Homogeneous nigre
	↓	13.0 14.0	11.0 12.0 13.0			Nigre + neat soap
	14.0	↓	↓			Nigre + lye
		15.0 16.0 17.0	14.0 15.0			Nigre + neat soap + lye
		18.0 19.0	16.0	13.0 14.0	10.0 11.0[b]	Neat soap + lye
		20.0 up to and incl. 24.0	17.0 up to and incl. 21.0	15.0 16.0	12.0[b] up to and incl. 16.0	Kettle wax or curd soap + lye
		25.0	22.0		17.0	Kettle wax or curd soap + lye + solid NaCl
	Sodium C_{12}-C_{18} alkyl sulphate			Sodium C_{14}-C_{18} alkyl sulphate		
% soap	5.0	10.0	20.0	5.0	10.0	
% NaCl added	10.0	10.0	8.0	6.5	6.0	Homogeneous nigre
		11.0	9.0 10.0		7.0	Nigre + neat soap
	11.0			7.0		Nigre + lye
		12.0 up to and incl. 15.0	11.0 12.0 13.0		8.0 up to and incl. 12.5	Nigre + neat soap + lye
		16.0 17.0 18.0	14.0 15.0		13.0	Neat soap + lye
		19.0 20.0 up to and incl. 24.0	16.0 17.0 up to and incl. 21.0		14.0[b] 15.0 up to and incl. 24.0	Kettle wax or curd soap + lye
		25.0	22.0		25.0	Kettle wax or curd soap + lye + solid NaCl

[b] See remark, Table I.

ter content to rise to 75-80%. At 50°C. the beginning of a similar phenomenon was observed when the NaCl content was made as high as possible. In that case the appearance of the neat soap changed, and the active matter content of the solid phase decreased (the volume increased). In the case of alkyl sulphates with higher molecular weight, where the margin between the concentration of salting-out and that of saturated NaCl is much wider (see later), this phenomenon at 50°C. was much more pronounced. These findings suggest the following possibiliites:

1. To the right of the 2-phase region neat soap-lye (I) (which is very small at 80°C.) there is a 3-phase region granular curd soap-neat soap-lye, and to the right of that region a 2-phase region curd soap-lye. The relatively low active matter content of the paste may be caused by embedded water phase.
2. Kettle wax is present instead of curd soap in the regions mentioned in (1). Kettle wax is a phase discovered (2) in the case of sodium stearate. It contained 60 to 70% of soap and a considerable amount of NaCl. McBain thought it very likely that this phase is also present in other fatty acid soaps.

It is very difficult to decide between these possibilities because solid-phase transformations always present great difficulties, mainly because in most cases phase separation is not possible. The safest method of investigation is vapor pressure determination. Some accurate vapor pressure measurements were therefore carried out in the case of sodium C_{10}-C_{18} alkyl sulphates, where the region to the right of the 3-phase region III is fairly broad. Differences in vapor pressure of 0.2 mm. Hg, corresponding with differences in concentration of 0.2% NaCl, could be detected. These measurements did not lead to the desired result however, because in order to obtain sufficient accuracy it is necessary to work at high alkyl sulphate contents (preferably about 60%) and in that case good mixing is nearly impossible. Therefore very long storage times are necessary to reach equilibrium conditions, which is not possible with alkyl sulphates at 50°C., owing to decomposition. Hence the only thing to be said about this region is that visual observations, *viz.*, the change from a translucent, doubly refracting plastic material to opaque, granular particles suspended in the liquid, make it sure that to the right of region I solid-phase transformations occur, implying that a 3-phase region with two solid soap phases must be present. It is not known however whether the second solid phase formed is granular curd soap or kettle wax.

b. *Influence of Molecular Weight.* With soaps of different molecular weights it was found that all phase diagrams are of the same type (Tables VI and VII and Figure 3). Only the most important parts of the diagrams were determined. In the sequence sodium C_8-C_{18}, C_{10}-C_{18}, C_{12}-C_{18}, and C_{14}-C_{18} alkyl sulphates the isotropic region greatly diminishes and the whole diagram is shifted to lower salt concentrations.

c. *Comparison with Pure Synthetic Sulphates and Sulphonates.* Most of these compounds were available only in small amounts. For comparison we considered it sufficient however to use only one concentration.

TABLE VII

Results of Synthetic Experiments with Sodium Alkyl Sulphates at 50°C.

Sodium C_{10}-C_{18} alkyl sulphate			Sodium C_{12}-C_{18} alkyl sulphate			Sodium C_{14}-C_{18} alkyl sulphate		
% soap	% NaCl	T_i	% Soap	% NaCl	T_i	% soap	% NaCl	T_i
1.9	13.1	78	2.0	10.9	77	2.0	6.6	40
2.0	13.1	37	2.0	10.8	32	2.0	6.7	59
4.0	13.4	86	5.0	11.0	>95	5.0	6.3	44
4.0	13.1	42	4.9	10.9	41	5.0	7.3	61
4.8	13.1	43	10.0	10.5	50	7.5	6.7	46
6.0	13.0	46	20.0	8.2	51	10.0	6.4	48
8.0	12.8	50	30.0	6.2	47	10.0	6.6	51
10.0	12.5	51	39.8	4.2	60	20.0	5.0	48
15.0	11.3	50	40.2	4.4	70	20.0	5.2	52
15.0	11.6	85	40.2	0	67	30.0	3.6	45
24.0	9.2	50				38.5	2.1	50
28.2	8.1	46				40.0	2.2	67
30.0	8.6	70				42.5	1.3	<20
38.0	5.2	26				44.0	1.4	>95
38.0	5.8	65				37.5	1.4	54
						32.4	0	<25
						32.8	0	>95

T_i = temperature in °C. at which isotropic solution separates a second phase.

We obtained the impression that the phase relations of these substances do not differ essentially from those of the mixed alkyl sulphates. With all pure compounds the three-phase region III was extremely small, as is the case with pure fatty acid soaps, so that in some cases it was impossible to detect it by direct means. The main results are given in Table VIII. The temperature had to be raised to attain a sufficient solubility (above the Kraft point).

TABLE VIII

Phase Boundaries of Various Synthetic Alkyl Sulphates

	Temperature °C.	Minimum concentration of NaCl needed for separation of 10% solutions into	
		Nigre and second phase	Neat soap and lye
		%	%
Sodium n-dodecyl-2-sulphate	70	17	21
Sodium n-tridecyl-1-sulphate	65	9	10½
Sodium n-tridecyl-2-sulphate	65	11½	14½
Sodium n-pentadecyl-2-sulphate	65	8	10½
Sodium n-hexadecyl-2-sulphate	70	....	7
Sodium n-tridecyl-1-sulphonate	65	11	12
Sodium n-dodecyl toluene sulphonate	75	7	9
Sodium sec. hexadecyl benzene sulphonate	75	4	....
Sodium C_8-C_{13} alkyl benzene sulphonates	65	5	7[c]
Sodium C_8-C_{18} alkyl sulphates	50	17½	20½
Sodium C_{10}-C_{18} alkyl sulphates	50	12½	17½
Sodium C_{12}-C_{18} alkyl sulphates	50	10½	15½
Sodium C_{14}-C_{18} alkyl sulphates	50	6½	13

[c] About.

It can be seen that the behavior of sodium tridecyl-2-sulphate and sodium pentadecyl-2-sulphate is similar to that of sodium C_{10}-C_{18} and C_{14}-C_{18} alkyl sulphates, respectively; the difference in temperature has only a minor influence.

In agreement with theoretical considerations the figures show that for phase separations:

1. the lower the molecular weight, the more NaCl is needed.
2. sodium tridecyl-2-sulphate needs more NaCl than sodium tridecyl-1-sulphate.
3. sodium tridecyl-1-sulphonate needs more NaCl than the corresponding sulphate.

From investigations with sodium dodecyl sulphonate (3) and hexanolamine oleate (4) it was found that the phase relations without the presence of salts were similar to those of fatty acid soaps. This gave further evidence for the suggestion made by Bernal and Crowfoot (5) and by Vold (3) that geometrical anisotropy of the molecules and a suitable balance in polar character between different atomic groupings are required for the formation of liquid crystalline phases.

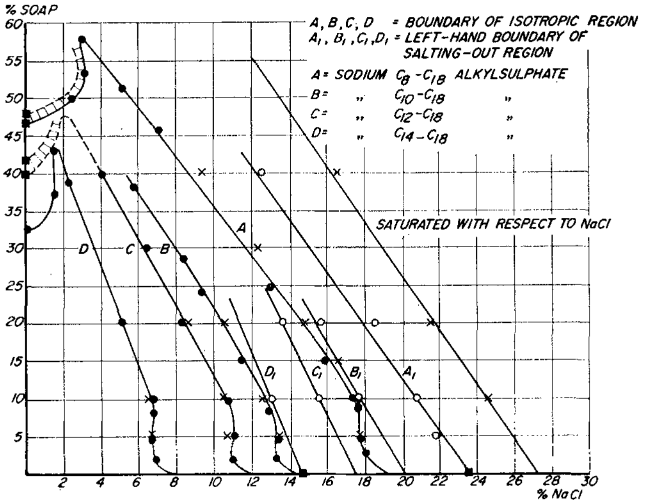

FIG. 3. Phase boundaries of alkyl sulphates, of different molecular weight, at 50°C.

- ● points on the boundary of the isotropic region calculated by the synthetic method
- × points on the boundary of the isotropic region and on the saturation line of NaCl calculated by the delimiting method
- ○ points on the left-hand boundary of the salting-out region calculated by the delimiting method
- ■ points calculated from analysis.

The present work shows that also with ternary mixtures, containing salt, there is a close correspondence in the phase relations of fatty acid soaps, alkyl sulphates, and alkyl or alkylarene sulphonates; it suggests that not only the formation of liquid crystalline phases but also the formation of two- and three-phase regions in ternary systems are controlled by geometrical anisotropy and the balance in polar character.

Summary

The phase behavior of ternary mixtures of various synthetic soaps, sodium chloride, and water are described. Several mixed sodium alkyl sulphates were investigated in detail at two temperatures; pure alkyl sulphates and alkyl and alkylarene sulphonates were investigated only tentatively. The phase relations showed a striking resemblance with those of fatty acid soaps.

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